OFFICE OF NAVAL RESEARCH

GRANT N0001493310058

R&T Code 4132083

Technical Report No. 1

Effect of Siloxane Segment Length on the Surface Composition of Polyimidesiloxane Copolymers and its Role in Adhesion

by

J. Zhao, S. R. Rojstaczer, J. X. Chen, M. Z. Xu and J. A. Gardella, Jr.

Prepared for Publication

in

Macromolecules

State University of New York at Buffalo
Department of Chemistry
Buffalo, NY

March 1998

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 1998	Technical

4. TITLE AND SUBTITLE
Effect of Siloxane Segment Length on the Surface Composition of Polyimidesiloxane Copolymers and its Role in Adhesion

5. FUNDING NUMBERS
GN0001493310058

6. AUTHOR(S)
Z. Zhao, S. R. Rojstaczer, J. X. Chen, M. Z. Xu and J. A. Gardella, Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry, NSM Complex
State University of New York, University at Buffalo
Buffalo, NY 14260-3000

8. PERFORMING ORGANIZATION REPORT NUMBER
98-01

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Navy, Office of Naval Research
800 North Quincy Street, Arlington, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
This document has been approved for public release and sale, its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

A series of polyimidesiloxane (SIM) copolymers, based on α,ω-aminopropylpoly-(dimethylsiloxane) (PDMS), 2,2-bis(4-[4-aminophenoxyl]phenyl)propane (BAPP) and 4,4'-oxydiphthalic-anhydride (ODPA) was synthesized in our laboratories. We investigated the effect of siloxane segment length on the surface composition of the SIM Copolymers and its role in adhesion. The aim is to elucidate the correlation between polymer structure, surface composition, and adhesion strength. Using a deconvolution computer program, composition-depth profiles of the near surface region to approximately 100 Å depth were simulated from the results of angle-dependent Eletron Spectroscopy for Chemical Analysis (ESCA) experiments. The simulated composition-depth profiles show that the topmost surface of the air (free) surface of the 75 μm thick SIM copolymer film consists of a siloxane-rich layer, even with the shortest siloxane segment. For a given siloxane bulk content, a longer siloxane segment gives a surface richer in siloxane. The adhesion strength was determined by peel strength testing of SIM Copolymers - Fe/Ni Alloy-42 laminates. The peel strength decreases exponentially with increasing thickness of the surface siloxane-rich layer, which corresponds to longer siloxane segment lengths. However, all values of adhesion strength of SIM copolymers are higher than that of pure polyimide. This confirms our previous results[1,2] that both siloxane and polyimide are essential components to rendering the high adhesion strength. The siloxane component provides a good diffusive ability, while the polyimide component interacts with the substrate to give rise to adhesion strength. Longer siloxane segments in the SIM copolymers are found to be detrimental to the adhesion strength by way of interference with the polyimide-metal interaction.

14. SUBJECT TERMS
Polymer Surface Composition, Polyimidesiloxane, Segment Length, ESCA.

15. NUMBER OF PAGES
36

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

Effect of Siloxane Segment Length on the Surface Composition of Polyimidesiloxane Copolymers and its Role in Adhesion

[1]J. Zhao, [2]S.R. Rojstaczer, [1]J.X. Chen, [2]M.Z. Xu and [1*]J.A. Gardella, Jr.

[1]Department of Chemistry, SUNY at Buffalo,

Buffalo, NY 14260-3000

[2]Technology Center, Occidental Chemical Corporation,

Grand Island, NY 14072

* Corresponding author

** Submitted to Macromolecules, March 1998

Abstract

A series of polyimidesiloxane (SIM) copolymers, based on α,ω-aminopropylpoly-(dimethylsiloxane)(PDMS), 2,2-bis(4-[4-aminophenoxyl]phenyl)propane(BAPP) and 4,4'-oxydiphthalic-anhydride(ODPA) was synthesized in our laboratories. We investigated the effect of siloxane segment length on the surface composition of the SIM copolymers and its role in adhesion. The aim is to elucidate the correlation between polymer structure, surface composition, and adhesion strength. Using a deconvolution computer program, composition-depth profiles of the near surface region to approximately 100Å depth were simulated from the results of angle-dependent Electron Spectroscopy for Chemical Analysis (ESCA) experiments. The simulated composition-depth profiles show that the topmost surface of the air (free) surface of the 75μm thick SIM copolymer film consists of a siloxane-rich layer, even with the shortest siloxane segment. For a given siloxane bulk content, a longer siloxane segment gives a surface richer in siloxane. The adhesion strength was determined by peel strength testing of SIM copolymers - Fe/Ni Alloy-42 laminates. The peel strength decreases exponentially with increasing thickness of the surface siloxane-rich layer, which corresponds to longer siloxane segment lengths. However, all values of adhesion strength of SIM copolymers are higher than that of pure polyimide. This confirms our previous results[1,2] that both siloxane and polyimide are essential components to rendering the high adhesion strength. The siloxane component provides a good diffusive ability, while the polyimide component interacts with the substrate to give rise to adhesion strength. Longer siloxane segments in the SIM copolymers are found to be detrimental to the adhesion strength by way of interference with the polyimide-metal interaction.

Keywords: Polymer Surface Composition, Polyimidesiloxane, Segment Length, ESCA.

Introduction

Polyimidesiloxane (SIM) copolymers are becoming increasingly important materials in microelectronic applications such as die attach adhesives, due to their attractive properties, such as good adhesion, low dielectric constant and low stress[1-17]. The surface characterization of SIM copolymers has also been of interest in regard to applications involving adhesion to flexible semiconductors[18].

The surface composition and properties of various SIM copolymers have been studied previously[3-8, 13-17]. Dwight et al.[4] measured the surface composition of a series of SIM copolymers by X-ray Photoelectron Spectroscopy (XPS or ESCA) and Transmission Electron Microscopy (TEM). They observed segregation of the lower surface energy siloxane segment at the copolymer surface with a bulk siloxane content up to 10%. In the bulk, microphase domains range from 100-400Å were observed. They studied the copolymers of dimethylsiloxane, 4,4'-oxydianiline(ODA) and 3,3',4,4'benzophenonetetracarboxylic-dianhydride (BTDA). McGrath et al.[5] investigated the effects of test temperature, molecular weight and siloxane content on the adhesive strength of SIM derived from BTDA and 3,3'-diaminodiphenyl-sulfone(DDS). Cho et al.[8] studied the factors governing the adhesion between pyromellitic dianhydride - 4,4'-oxydianiline(PMDA-ODA) copolymer and glass. They found that the adhesion energy increases with an increase in PDMS bulk content.

In recent years, the Occidental Chemical Corporation (OxyChem®) developed and commercialized a series of adhesives, based on SIM copolymers, for microelectronic applications. Work from our laboratories by Zhuang et al.[1] used ESCA to study the surface composition of a series of commercially available (OxySIM™) SIM copolymers based on a proprietary mixed imide structure with different processing variations and different PDMS bulk content and segment length. They found that small amount of PDMS and short siloxane segments in the SIM copolymers yield a surface region with both PDMS and polyimide components. The adhesion strength of the SIM series was evaluated by peel tests on Fe/Ni Standard Alloy-42 and correlated to the surface structure and bulk composition of the SIM copolymers. In particular, the highest adhesion strength comes from the SIM copolymer with only one dimethylsiloxane repeat unit. This result suggested that both PDMS and polyimide are essential components to obtain good adhesion. PDMS has a good diffusive ability and readily reaches the substrate upon being pressed, so as to achieve intimate contacts. Imide groups interact with the substrate presumably through strong chemical interactions. However, the detailed structure of the SIM copolymers studied was not divulged[1]. In order to quantitatively understand the effects of segment length and bulk composition on the surface composition and morphology of SIM copolymers, a study of a series of known structure SIM copolymers has been carried out in the present work.

In many phase separated copolymer systems, the thermodynamic driving force for minimizing the total free energy of the system results in preferential surface segregation of the lower surface energy constituent. However, the extent and in-depth distribution of surface

segregation in copolymers are affected by a number of other factors. These factors include bulk composition[19, 20], block length[21, 22], processing conditions (annealing[19, 20, 22-24], casting solvent[20, 23, 25], etc.) and block sequence distribution[26], etc. In a preliminary report[2] on the system under study, a series of polyimidesiloxane (SIM) copolymers, based on α,ω-aminopropylpoly-(dimethylsiloxane)(PDMS), 2,2-bis-(4-[4-aminophenoxyl]phenyl)-propane(BAPP) and 4,4'-oxydiphthalic-anhydride(ODPA) was synthesized in our laboratories. The effects of siloxane segment length (average number of dimethylsiloxane repeat units = 1, 2, 3, 4, 5, and 9) and siloxane bulk content (1~30wt%) on the surface composition and morphology of the SIM copolymers were investigated. In all cases, siloxane component was segregated to the topmost air (free) surface of the *ca.*75μm thick film, even with short siloxane segments and low PDMS bulk contents. Angle-dependent ESCA measurements show that the dominant factor in defining the surface composition is not the bulk composition, but rather the siloxane segment length. For a given PDMS bulk content, a longer siloxane segment gives a surface richer in PDMS, while for a given siloxane segment length, varying the PDMS bulk content does not significantly change the surface composition. However, a full analysis of the effect of siloxane segment length on the composition-depth profile and its role in adhesion was not complete.

Experimentally varying the angle of the sample plane with respect to the analyzer yields different information depths (known as angle-dependent ESCA). However, the result from angle-dependent ESCA is not a direct in-depth profile of composition as a function of depth because all atoms within the path of the probing X-ray contribute to the signal but the contribution of each decreases exponentially with the distance from the free surface[27]. To obtain the composition-

depth profiles from the angle-dependent ESCA data, deconvolution methods have been used by our research group[21, 28] as well as others[29-34]. In the present work, a deconvolution program[21] was utilized to obtain composition-depth profiles from the angle-dependent ESCA results. This program assumes a model of surface segregation and boundary conditions based on the bulk composition. In particular, the effect of siloxane segment length (average number of dimethylsiloxane repeat units = 1, 2, 3, 4, 5, and 9) on the surface composition of the SIM copolymers with 10wt% PDMS bulk content, a subset of the materials studied previously[2], and its role in adhesion is presently investigated. The aim is to elucidate the correlation between polymer structure, surface composition, and adhesion strength. The adhesion strength was measured by peel test of SIM copolymers laminated on Fe/Ni Alloy-42.

Experimental

Sample preparation

The SIM copolymers for this study were prepared by the two-stage polyamic acid method. The overall scheme of sample preparation is shown in Scheme 1. First, α,ω-aminopropylpoly(dimethylsiloxane)(PDMS) (PCR, Inc.) was added, with stirring, to 2,2-bis(4-[4-aminophenoxyl]phenyl)propane(BAPP) (WCK, Co.) in a combined solvent with 4:1 of 1-Methyl-2-Pyrrolidinone(NMP) and Toluene. Then, 4,4'-oxydiphthalic-anhydride(ODPA) (Oxychem, Co.) was added slowly, with stirring, to the above mixture. Different siloxane segment lengths in the SIM copolymers resulted from varying the p value in Scheme 1. Different copolymer bulk compositions (PDMS contents) resulted from varying the m/n ratio in Scheme 1.

PDMS with average molecular weights (M_w) of 252, 334, 406, 475, 550 and 813 g/mol were used, corresponding to p = 1, 2, 3, 4, 5 and 9 in Scheme 1. The value of p represents an average segment length except 1. In the present work, the PDMS content was kept constant at 10wt% and the different siloxane segment length was determined by the M_w of the siloxane-diamine monomer. The reaction mixture was stirred at room temperature for 20hrs. The resulting polyamic acid solutions were drawn to Silicone-treated PET film substrates with a doctor-blade. The coated films were then placed in an oven at 70°C and heated to 250°C at a rate of 5°C/min and then held at 250°C for 60 minutes. The thickness of the imidized film was in the range of ~60-90μm. The air sides of the resulting thick films were analyzed by ESCA so as to determine the surface composition of the SIM copolymers. The specimens were denoted as G-X, where X represents the average siloxane segment length. The bulk N/Si and C/N values that were calculated from the starting materials are shown in Table 1.

ESCA

ESCA analysis was carried out in a Physical Electronic/PHI 5300 X-ray Photoelectron Spectrometer operated at 300W(15kV and 20mA). MgKα radiation (1253.6eV) and pass energy of 89.45eV for survey as well as 17.9eV for high-resolution acquisition was used for all angle-dependent acquisitions. Binding energies were calibrated by setting C1s at 285.0eV. Photoelectron emission take-off angles of 10°, 30°, 45°, 90° were used for all samples. Signals from all four detectable elements (carbon, oxygen, nitrogen and silicon) were recorded. For quantification, ESCA atomic sensitivity factors (ASF) relative to F1s = 1.00 were used. The ASF

applied are 0.27 for Si2p, 0.42 for N1s, 0.66 for O1s and 0.25 for C1s[35, 36]. The concentration of each element was obtained from the ESCA signal area divided by the corresponding ASF. Si is selected to signify the siloxane component in the SIM copolymer and the intensity of the Si2p peak is used to monitor the relative concentration of PDMS. Similarly, N is selected to represent the polyimide component in the SIM copolymer and the intensity of the N1s peak is used to monitor the relative concentration of polyimide.

Peel test

The samples for the adhesion strength test are strips (1/4"x1" or 6.3mmx25mm) of the SIM copolymers. They were laminated onto Fe/Ni Alloy-42 substrates at 350± 10°C with 250lb pressure applied for 1 minute. The Fe/Ni Alloy-42 was ultrasonically cleaned with methylene dichloride three times. The peel tests were performed on a Diventro Peel Tester adapted with a 5kg Omega Digital Force Gauge connected to a strip chart recorder. The test was done in 90° geometry. The peel rate was 40mm/min.

Table 2 shows the glass transition temperatures (T_g) of the SIM copolymers as a function of siloxane segment length at a constant 10wt% siloxane bulk content. It is clear that the T_g of polyimidesiloxane copolymers increases with increasing the siloxane segment length. This is consistent with our previous results[37]. This effect is likely due to the smaller extent of interphase mixing associated with the longer blocks of siloxane and polyimide segments[38, 39].

In general, the difference between the lamination temperature (T_l) of adhesion strength measurements and the glass transition temperature (T_g) of the copolymer is kept at a constant value and the best adhesion strength usually comes from a temperature range of (T_l-T_g) ≅100-200°C. In our cases, SIM copolymer G-1 reached its highest adhesion strength at 350°C, while other SIM copolymers, such as G-4, G-5, and G-9, flowed severely at lamination temperatures higher than 350°C and resulted in poor adhesion strength. Considering the variation of the T_g of the SIM copolymers (Table 2), a constant lamination temperature of 350°C, which is within the temperature range to obtain the best adhesion strength for all the SIM copolymers, was used in all the adhesion strength measurements.

Recovery of the composition-depth profiles from angle-dependent ESCA data

The principle of revealing the composition-depth profiles of the SIM copolymers is the same as that described in reference 21. The intensities of the photoelectronic response from carbon and nitrogen atoms as functions of the photoelectron take-off angle can be formulated in the derivative as

$$dI_C(\theta) = F\alpha_C N_C(x) K e^{-x/(\lambda_C \sin\theta)}\, dx \qquad (1)$$

$$dI_N(\theta) = F\alpha_N N_N(x) K e^{-x/(\lambda_N \sin\theta)}\, dx \qquad (2)$$

where I is the detected intensity of photoelectrons from a given atom, subscripts C and N denote carbon and nitrogen, respectively, θ is the photoelectron take-off angle, F is the X-ray flux, α is the cross-section of photoionization in a given shell of a given atom for a given X-ray energy, N(x) is the depth profile of the atomic density, x is the vertical distance from the free surface, K

is a spectrometer factor, and λ is the inelastic mean free path of the electrons. The inelastic mean free paths (IMFP) for C1s and N1s were calculated with the modified Bethe equation[40]. The resultant IMFPs of C1s and N1s electrons are about 18Å and 17Å, respectively, for all the synthesized SIM copolymers with an estimated density of 1.33g/cm^3.

Assuming F, K, and α are independent of x and define normalized intensity I'(θ) as I(α)/(FαK), one can integrate equations 1 and 2 and obtain

$$I_C'(\theta) = I_C(\theta)/(F\alpha_C K) = \int_0^\infty N_C(x) e^{-x/(\lambda_C \sin\theta)}\, dx \qquad (3)$$

$$I_N'(\theta) = I_N(\theta)/(F\alpha_N K) = \int_0^\infty N_N(x) e^{-x/(\lambda_N \sin\theta)}\, dx \qquad (4)$$

or

$$I_C'(\theta)/I_N'(\theta) = [\int_0^\infty N_C(x) e^{-x/(\lambda_C \sin\theta)} dx]/[\int_0^\infty N_N(x) e^{-x/(\lambda_N \sin\theta)} dx] \qquad (5)$$

Normalized intensities for different atoms at a photoelectron take-off angle θ, usually reported as a ratio, such as I_C'/I_N', can be obtained from the ESCA data, as corrected by Vargo and Gardella[36].

In the previous work using this deconvolution method[21], the poly(dimethylsiloxane-urethane) (PDMS-PU) segmented copolymer chains are divided into PDMS soft segments and PU hard segments. Since nitrogen is unique to the PU hard segments, the weight percentage of PDMS (soft segment) or PU (hard segment) can be calculated from the atomic ratio of Carbon to nitrogen (C/N). The reason that using the ratio of photoelectron intensities of carbon to nitrogen to calculate the PDMS surface concentration is due to the relatively large variation in nitrogen

signal at different photoelectron take-off angle, while the variation of silicon signal is within the experimental error. In the present work, the SIM copolymer chains are similarly divided into siloxane soft segments and polyimide hard segments. Assuming that changes in density throughout the film (<5%) and the difference between weight fraction and volume fraction values (<3%) are negligible and given $\upsilon(x)$ is the depth profile of the polyimide hard segments, the atomic depth profiles for carbon and nitrogen are

$$N_C(x) = \eta\upsilon(x) + \sigma(1-\upsilon(x)) \tag{6}$$

$$N_N(x) = \eta\upsilon(x)\gamma \tag{7}$$

The weight fraction (C) of polyimide hard segments, the number density (η) of carbon atoms in the polyimide hard segments, the number density (σ) of carbon atoms in the siloxane soft segments, and the atomic ratio (γ) of N/C in polyimide hard segments for different SIM copolymers were calculated and summarized in Table 3.

A Gaussian distribution model with four-parameter was constructed to simulate the volume fraction $\upsilon(x)$ of polyimide hard segments

$$\begin{aligned} \upsilon(x) &= C \cdot H \cdot \exp[-0.5(x-L)^2/S_1^2] && x \le L \\ &= C \cdot \{1+(H-1) \cdot \exp[-0.5(x-L)^2/S_2^2]\} && x > L \end{aligned} \tag{8}$$

where H is a parameter relevant to the magnitude of the trough in the profile, x is the distance from the free surface (in Å), L is the location of the trough in the profile, S_1 characterizes the shape of the profile to the left of the trough, and S_2 characterizes the shape of the profile to the right of the trough, and C is the volume fraction of polyimide hard segments in the bulk (again, assuming the difference between weight fraction and volume fraction values is negligible).

The ratio of the intensities of photoelectrons from carbon and nitrogen, designated as R, can be calculated using equation 5 by inserting equations 6-8 and adjusting the four variables in the equation 8. This result is then compared with the data from angle-dependent ESCA experiments.

To reach the optimal values of these four variables, the following objective function was used.

$$\psi = \{(1/n)\sum^{n}[[R_{cal}(H, L, S_1, S_2) - R_{exp}(\theta_n)]/R_{exp}(\theta_n)]^2\}^{1/2} \qquad (9)$$

where n is the number of photoelectron take-off angles. The optimization was achieved using the algorithm developed by Dr. Tai Ho[21] and programmed in Mathcad 5.0 (MathSoft, Inc.). For each sample of a particular segment length at constant 10wt% bulk content, four replicates of angle-dependent ESCA analysis were averaged at each angle to obtain $R_{exp}(\theta)$. Error estimates leading to error bars are the result of the variance from the fitting of the optimum objective functions (equation 9).

Results and Discussion

Surface composition

Figure 1 is a plot of N/Si ratio detected from ESCA versus the sinθ (θ is the angle of detector with respect to the sample surface plane). It shows the influence of siloxane segment length on the surface composition of the SIM copolymers, where the atomic ratio of nitrogen to

silicon is used to represent the surface composition. In all cases, the N/Si values detected at the surface and reported in Figure 1 are much smaller than the corresponding bulk values (see Table 1). This indicates that siloxane component was segregated to the topmost surface of the air (free) surface of the as-prepared thick film. The N/Si ratio decreases linearly with the decrease of $\sin\theta$. This suggests that the PDMS concentration decreases with depth, while the polyimide concentration increases. All the y-intercepts approach zero with decreasing of $\sin\theta$ towards zero, which implies that only a small amount or no polyimide exists at the sampling depth equal to zero (*i.e.* the topmost surface). In particular, it is noted that the N/Si ratio decreases with increasing siloxane segment length at a given $\sin\theta$. In other words, with the same PDMS bulk content in the SIM copolymers, a longer siloxane segment gives a surface richer in PDMS.

Table 4 gives the atomic ratio of C/N in the SIM copolymers obtained by angle-dependent ESCA experiments. Figure 2 shows the composition-depth profiles for the siloxane component in each copolymer recovered from these atomic percentage ratios of C/N, utilizing the deconvolution method described above. These composition-depth profiles reveal some features that are not obvious in the raw ESCA data. First, it is clear that siloxane was segregated to the sample surface forming a topmost siloxane-rich layer. This topmost siloxane-rich layer is followed by a siloxane depletion region. This is an inherent result of the assumed boundary conditions. It is assumed that any surface excess layer of the siloxane segment must necessarily be balanced by a siloxane depletion layer, because the average composition of the siloxane segment integrated over one polymer chain length must equal to its bulk composition[21, 28]. Scheme 2 shows the proposed surface structure of the backbone of the SIM copolymers. It

demonstrates the siloxane-rich region and siloxane depletion region, though the real surface statistically consists of all the possible surface configurations of the backbone of SIM copolymers.

This analysis allows a second way to extrapolate the surface composition at zero sampling depth from these profiles. Figure 3(a) shows the volume fractions of siloxane component at the very top surface (sampling depth equal to zero) for these SIM copolymers. With the same 10wt% PDMS bulk content, the very top PDMS surface coverage varies from 0.889 to 0.993 with increasing of the siloxane segment length, dimethylsiloxane repeat units equal to 1, 2, 3, 4, 5 to 9. The very top PDMS surface coverage increases exponentially with increasing siloxane segment length. This confirms our suggestion that only a small amount or no polyimide component exists at zero sampling depth of these SIM copolymers.

Of particular interest is the thickness of the siloxane-rich layer defined as the depth from the very top surface to where the PDMS volume fraction reaches its bulk content. Figure 3(b) shows the thickness of the siloxane-rich layer with variation of siloxane segment length. With the same 10wt% PDMS bulk content, varying the siloxane segment length, dimethylsiloxane repeat units equal to 1, 2, 3, 4, 5 to 9, gives a thickness (±5%) of surface siloxane-rich layer of 4.4, 5.6, 6.5, 7.3, 8.0 and 8.6Å, respectively. This is to say that, for a given PDMS bulk content in the SIM copolymers, a longer siloxane segment gives a thicker siloxane-rich layer at the sample surface. The thickness of the surface siloxane-rich layer also increases exponentially with increasing of the siloxane segment length.

The thickness of surface siloxane-rich layer recovered from the deconvoluted composition-depth profiles is comparable with the chain dimensions of the siloxane segments. Figure 4 shows the comparison of the thickness of surface siloxane-rich layer and the average chain dimensions of siloxane segment calculated from a free-jointed chain model and also a short range effects model[41]. The bond length of Si-O in PDMS of 1.64Å[42, 43] was used in the calculation. To simplify the calculation, the chain dimension values of the siloxane segments from the short range effects model were calculated using either the bond angle of Si-O-Si in PDMS of ~143° or the bond angle of O-Si-O in PDMS of ~110°[42, 43]. The real values of the chain dimensions of the siloxane segments from the short range effects model must be between the above two calculated values. While the siloxane segment length equals to 1 or 2 dimethylsiloxane units, the thickness of surface siloxane-rich layer is between the chain dimension values calculated by the free-jointed chain model and the short range effects model. This is because the expansion of a covalently bonded polymer chain is restricted by the bond angles between each chain atom[42]. The short range effects become more significant towards shorter chains, though the short range effects model may not be appropriate with extremely short siloxane segments such as dimethylsiloxane repeat units equal to 1 or 2. With increasing siloxane segment length, the PDMS chain gets more freedom, especially[42] with Si-O bond length of 1.64Å which is significant longer than that of C-C bond (1.53Å) of general polymer skeletal bond and Si-O-Si bond angle of ~143° which is more open than the usual tetrahedral bond angle of ~109°. This is the confirmation that, with increasing siloxane segment length, the thickness of surface siloxane-rich layer approaches the chain dimension value calculated by the free-jointed chain model.

Adhesion strength

The adhesion strength measured by peel test of SIM copolymers laminated to Fe/Ni Alloy-42 was plotted against the recovered thickness of surface siloxane-rich layer in Figure 5. It shows that the adhesion strength, ranging from 1.35kg/cm of G-1 to 0.50kg/cm of G-9, decreases exponentially with increasing of the thickness of surface siloxane-rich layer, though the adhesion strengths of all SIM copolymers are greater than that of pure polyimide polymer (0.25kg/cm). This is evidence that both PDMS and polyimide are essential components to rendering high peel strength. In order to achieve high adhesion strength, there must be a component in the adhesive that presumably interacts with the substrate through strong chemical interactions (*i.e.* polyimide). However, it is equally important to have sufficient diffusive ability or ductility for the adhesive to achieve intimate contact with substrate[44]. PDMS has a good diffusive ability and readily reaches the substrate upon being pressed, so as to achieve intimate contacts. Imide groups interact with the substrate presumably through strong chemical interactions, so as to achieve adhesion. A longer siloxane segment in the SIM copolymers hinders the efficacy of adhesion due to a thicker siloxane-rich surface layer. This hindrance effect increases exponentially with increasing of the thickness of the surface siloxane-rich layer, which is determined by the siloxane segment length in the SIM copolymers.

As in our previous work[1], the adhesion strength was also plotted against the N/Si atomic ratio determined by angle-dependent ESCA in Figure 6. The justification for using the ESCA data at photoelectron take-off angle equal to 90° is because the lamination of the SIM copolymers for subsequent peel test was done by hot pressing at 250lb pressure and 350°C, which means that

a thick surface region is likely involved in the adhesion process. It is interesting to note that the adhesion strength increases linearly with increasing of N/Si atomic ratio, where a larger N/Si ratio corresponds to a sample with a smaller amount of PDMS at the surface. This confirms our suggestion that a shorter siloxane segment in the SIM copolymer results in a smaller amount of PDMS in the near surface volume and gives stronger adhesion.

Conclusions

We investigated the effect of siloxane segment length on the surface composition of the SIM copolymers and its role in adhesion with the aim to elucidate the correlation between polymer structure, surface composition, and adhesion strength. Composition-depth profiles of the near surface region to approximately 100Å depth were simulated from the angle-dependent ESCA results. The simulated composition-depth profiles show that the topmost surface of the air (free) surface of the *ca.*75μm thick SIM film was covered by a siloxane-rich layer, even with the shortest siloxane segment. Both the very top PDMS surface coverage (sampling depth equal to zero) and the thickness of the surface siloxane-rich layer increase exponentially with increasing of the siloxane segment length in the SIM copolymers. The adhesion strength measured by peel strength testing of SIM copolymers laminated to Fe/Ni Alloy-42 decreases exponentially with increasing of the thickness of the surface siloxane-rich layer, corresponding to longer siloxane segment length, though all values of the adhesion strength of SIM copolymers are higher than that of pure polyimide. This confirms our previous results that both PDMS and polyimide are essential components to rendering high adhesion strength. PDMS component provides a good

diffusive ability, while imide component interacts with the substrate to give rise to adhesion strength. A longer siloxane segment in the SIM copolymers hinders the efficacy of adhesion due to a thicker siloxane-rich surface layer.

Acknowledgement:

JZ and JAG acknowledge support from The Office of Naval Research.

References:

(1) H.Z. Zhuang, J.A. Gardella, Jr., J.A. Incavo, S. R. Rojstaczer, J.C. Rosenfeld, J. Adhesion **1997**, 63, 199.

(2) J. Zhao, S.R. Rojastaczer and J.A. Gardella, Jr., J. Vac. Sci. Technol. (in press).

(3) V.H. Kuckertz, Macromol. Chem. **1996**, 4-5, 212.

(4) D. Dwight, J. McGrath, G. Lawson, N. Patel, and G. York, Contemp. Top. Poly. Sci. **1989**, 6, 265.

(5) T.H. Yoon, C.A. Arnold-McKenna and J.E. McGrath, J. Adhesion **1992**, 39, 15.

(6) M.C. William and R. Spontak, Polymer Journal **1988**, 20, 649.

(7) M.C. William and R. Spontak, J. Appl. Poly. Sci. **1989**, 38, 1607.

(8) K. Cho, D. Lee, K.H. Seo and T.O. Ahn, ANTEC **1995**, 2889.

(9) A. Berger, U.S. Pat. 4,395,527 1983.

(10) C.J. Lee, U.S. Pat. 4,670,497 1987.

(11) S.R. Rojstaczer, U.S. Pat. 5,209,981.

(12) S.R. Rojstaczer, D.Y. Tang and J.A. Tyrell, U.S. Pat. 5,317,049.

(13) F.L. Keohan and J.E. Hallgren, *Silicon-Based Polymer Science: A Comprehensive Resource*, J.M. Zeigler, ed., American Chemical Society, 1990, p165.

(14) N. Furukawa, Y. Tamada, M. Furukawa, M. Yuasa and Y. Kimura, J. Poly. Sci. Part A-Polymer Chemistry **1997**, 35, 2239.

(15) Y. Yamada and N. Furukawa, Polymer Journal **1997**, 29, 923.

(16) J.L. Hedrick, H.R. Brown, W. Volksen, M. Sanchez, C.J.G. Plummer and J.G. Hilborn, Polymer **1997**, 38, 605.

(17) W. Volksen, J.L. Hedrick, T.P. Russell and S. Swanson, J. Appl. Poly. Sci. **1997**, 66, 199.

(18) M.H. Na, J. Haetty, J. Zhao, H.C. Chang, E.H. Lee, H. Luo, A. Petrou and J.A.Gardella, Jr., Proceedings of Fourth International Conference on Frontiers of Polymers and Advanced Materials, Cairo, Egypt, January, 1997.

(19) X. Chen, H.F. Lee, and J.A. Gardella, Jr., Macromolecules **1993**, 26, 4601.

(20) X. Chen, J.A. Gardella, Jr., and R.E. Cohen, Macromolecules **1994**, 27, 2206.

(21) X. Chen, J.A. Gardella, Jr., T. Ho, and K.J. Wynne, Macromolecules **1995**, 28, 1635.

(22) X. Chen, J.A. Gardella, Jr., and P.L. Kumler, Macromolecules **1993**, 26, 3778.

(23) H.Z. Zhuang and J.A. Gardella, Jr., Macromolecules **1997**, 30, 3632.

(24) G. Coulon, T.R. Russell, V.R. Deline and P.F. Green, Macromolecules **1989**, 22, 2581.

(25) H.R. Thomas and J.J. O'Malley, Macromolecules **1979**, 12, 323.

(26) L. Li, C.M. Chan, and L.T. Weng, Macromolecules **1997**, 30, 3698.

(27) D.T. Clark, Adv. Polym. Sci. **1977**, 24, 126.

(28) H.Z. Zhuang, K.G. Marra, T. Ho, T.M. Chapman, and J.A. Gardella, Jr., Macromolecules **1996**, 29, 1660.

(29) M. Pijolat and G. Hollinger, Surf. Sci. **1977**, 24, 126.

(30) H. Iwasaki, R. Nishitani and S. Nakamura, Jpn. J. Appl. Phys. **1978**, 17, 1519.

(31) P.H. Holloway and T.D. Bussing, Surf. Interface Anal. **1992**, 18, 251.

(32) V.I. Nefedov and O.A. Baschenko, J. Electron Spectrosc. Relat. Phenom. **1988**, 47, 1.

(33) B.J. Tyler, D.G. Castner and B.D. Ratner, Surf. Interface Anal. **1989**, 14, 443.

(34) R. Jisl. Surf. Interface Anal. **1990**, 15, 719.

(35) *Handbook of X-Ray Photoelectron Spectroscopy,* Perkin-Elmer Corporation, 1979.

(36) T.G. Vargo and J.A. Gardella, Jr., J. Vac. Sci. Technol. **1989**, A7, 1733.

(37) S.R. Rojstaczer, J.A. Tyrell and D.Y. Tang, unpublished results.

(38) S.J. Clarson, *Siloxane Polymers*, S.J. Clarson, ed., PTR Prentice Hall, Inc., 1993, p218.

(39) J.J. Kennan, *Siloxane Polymers*, S.J. Clarson, ed., PTR Prentice Hall, Inc., 1993, p108.

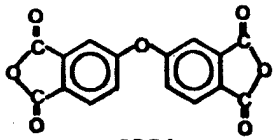
(40) S. Tanuma, C.J. Powell and D.R. Penn, Surf. Interface Anal. **1993**, 21, 165.

(41) J.M.G. Cowie, *Polymers: Chemistry & Physics of Modern Materials 2nd*, Blackie and Son Limited, 1991, p215.

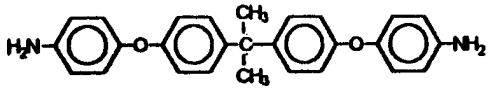
(42) J.E. Mark, *Silicon-Based Polymer Science: A Comprehensive Resource*, J.M. Zeigler, ed., American Chemical Society, 1990, p47.

(43) M.J. Owen, *Siloxane Polymers*, S.J. Clarson, ed., PTR Prentice Hall, Inc., 1993, p333.

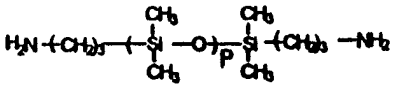
(44) S. Wu, *Polymer Interface and Adhesion*, Marcel Dekker, Inc. New York and Basel, p337.



ODPA



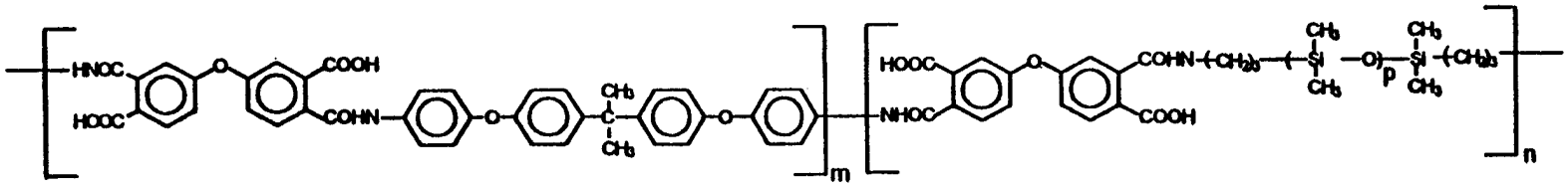
BAPP



Aminopropyl terminated PDMS

Solid Content 25%

NMP/Toluene (4:1), Room Temp. With stirring 16hr



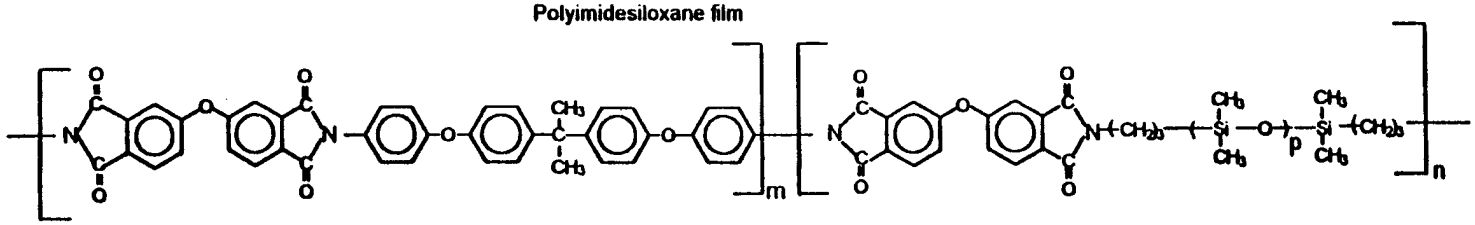
Polyamic acid

Coating on Si Slide

Drying, 80° C, 10min

Curing, 250° C, 1hr

Polyimidesiloxane film



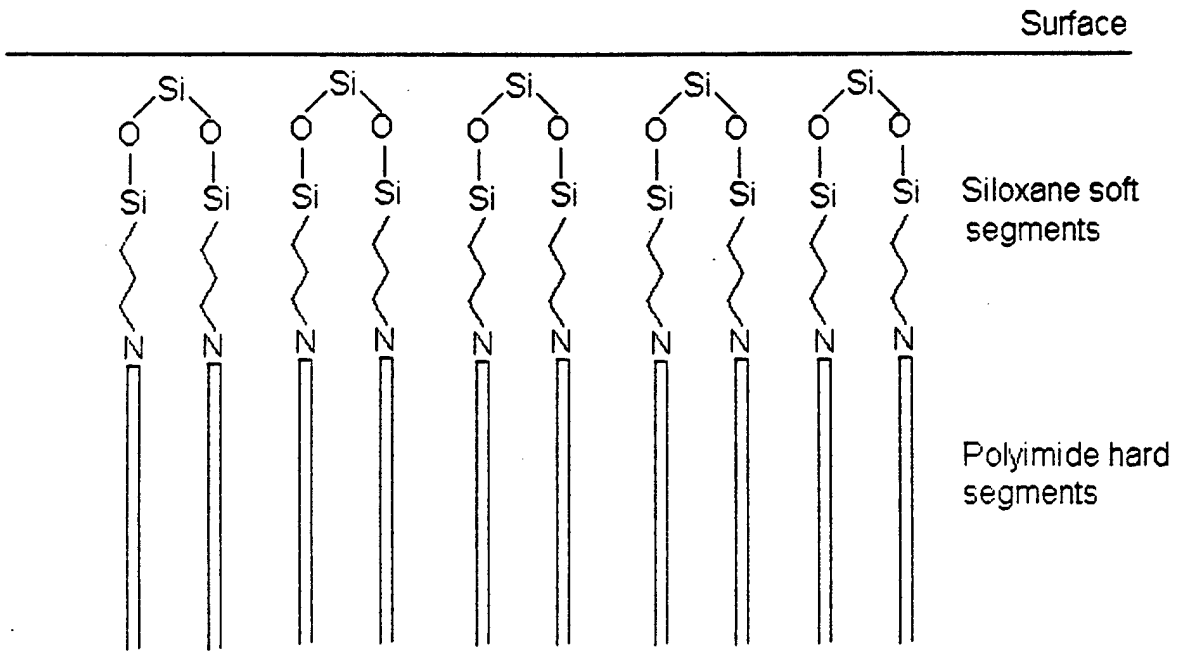

Surface
Siloxane soft segments
Polyimide hard segments

Table 1. The N/Si and C/N values of the bulk copolymers.

#	G-1	G-2	G-3	G-4	G-5	G-9
N/Si	3.67	3.16	2.86	2.60	2.45	2.14
C/N	18.09	18.75	18.92	19.09	19.52	20.09

Table 2. Glass transition temperature of the SIM copolymers with variation of siloxane segment length for a given 10wt% PDMS bulk content.

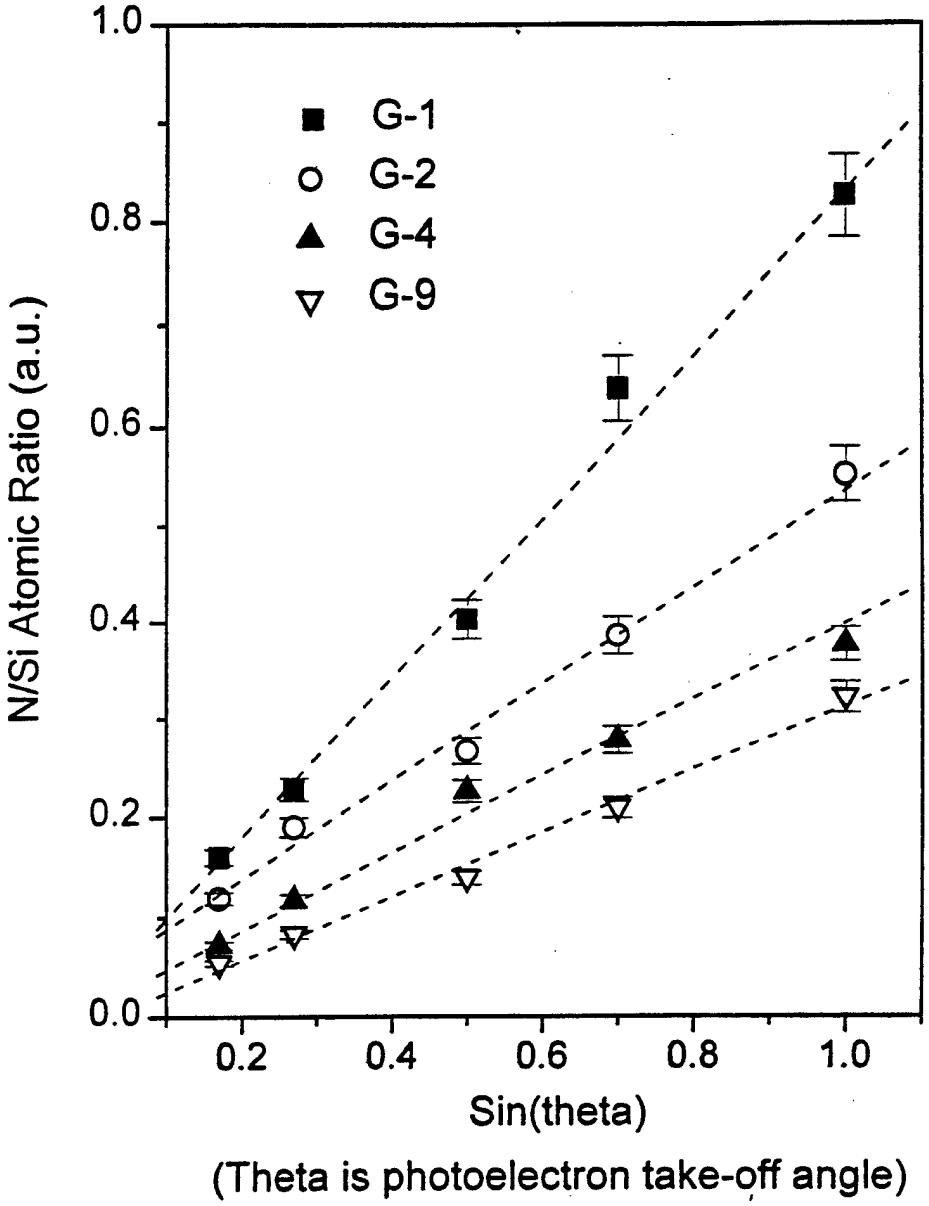
#	G-1	G-2	G-3	G-4	G-5	G-9
T_g (°C)	165	170	178	171	190	210

Table 3. Parameters used in recovering the composition-depth profiles.

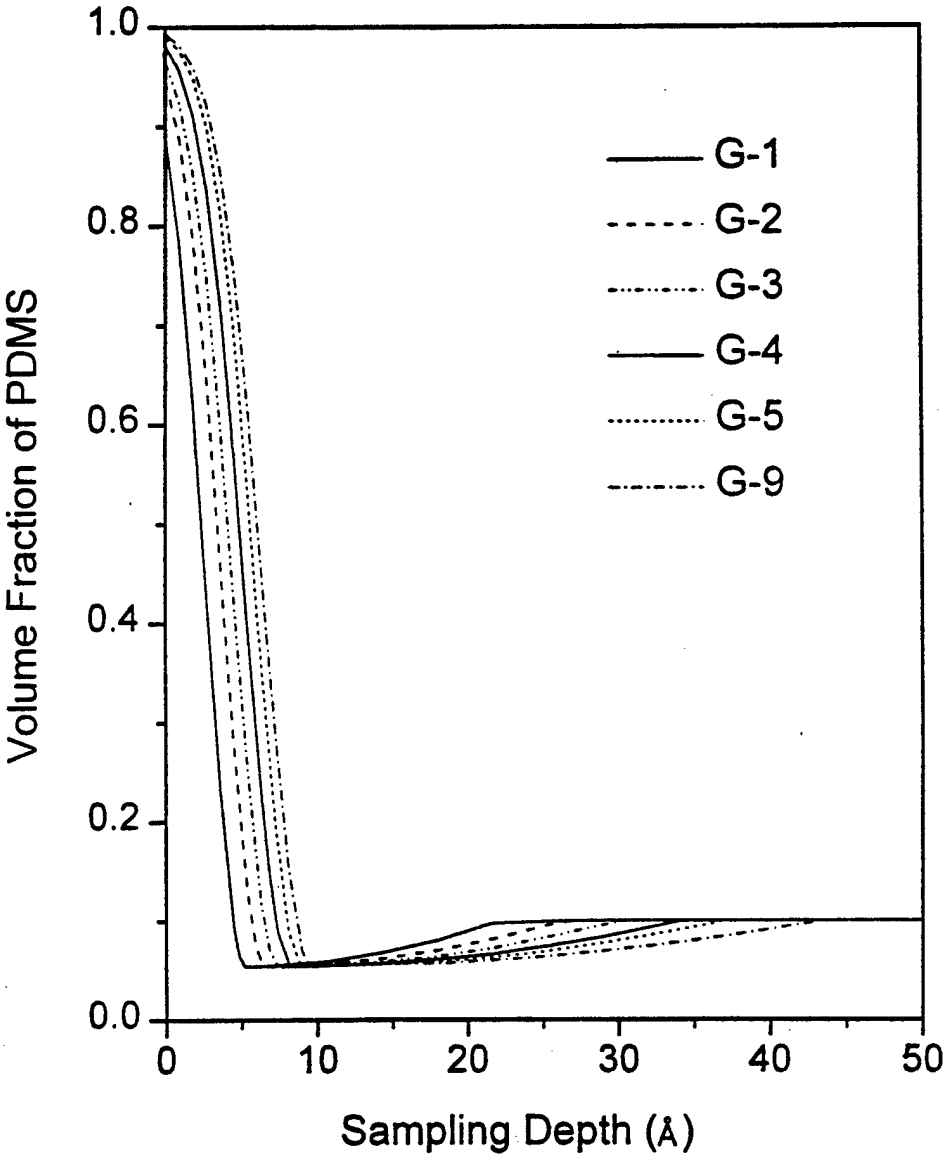
#	G-1	G-2	G-3	G-4	G-5	G-9
C	0.90	0.90	0.90	0.90	0.90	0.90
η	61.90	62.22	62.43	62.58	62.69	62.93
σ	46.30	41.38	38.46	36.53	35.16	32.18
γ	0.0560	0.0536	0.0523	0.0515	0.0508	0.0494

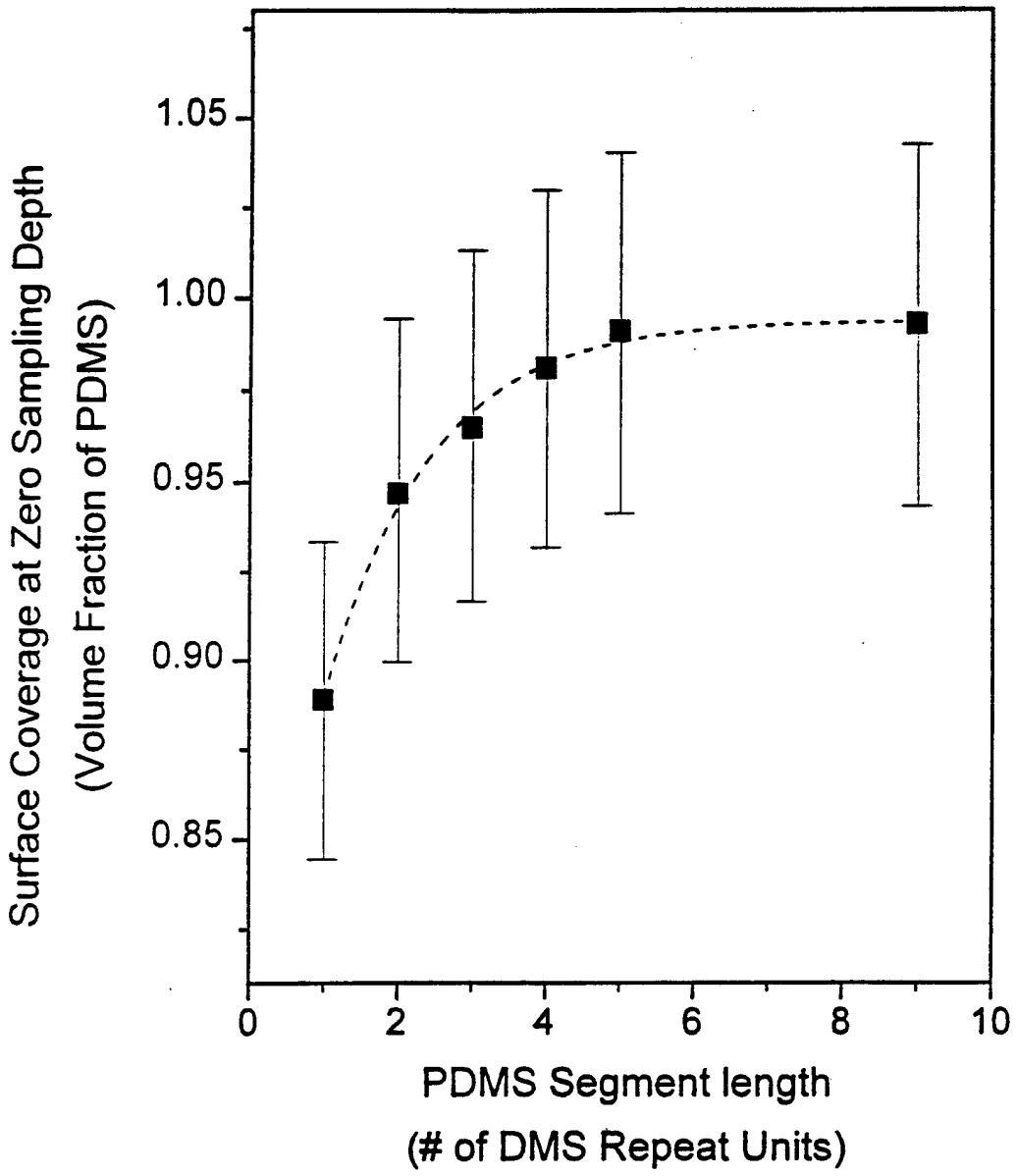
Table 4. Atomic ratio of C/N in the SIM copolymers (±5%), determined by angle-dependent ESCA as reflected by peak ratios prior to deconvolution.

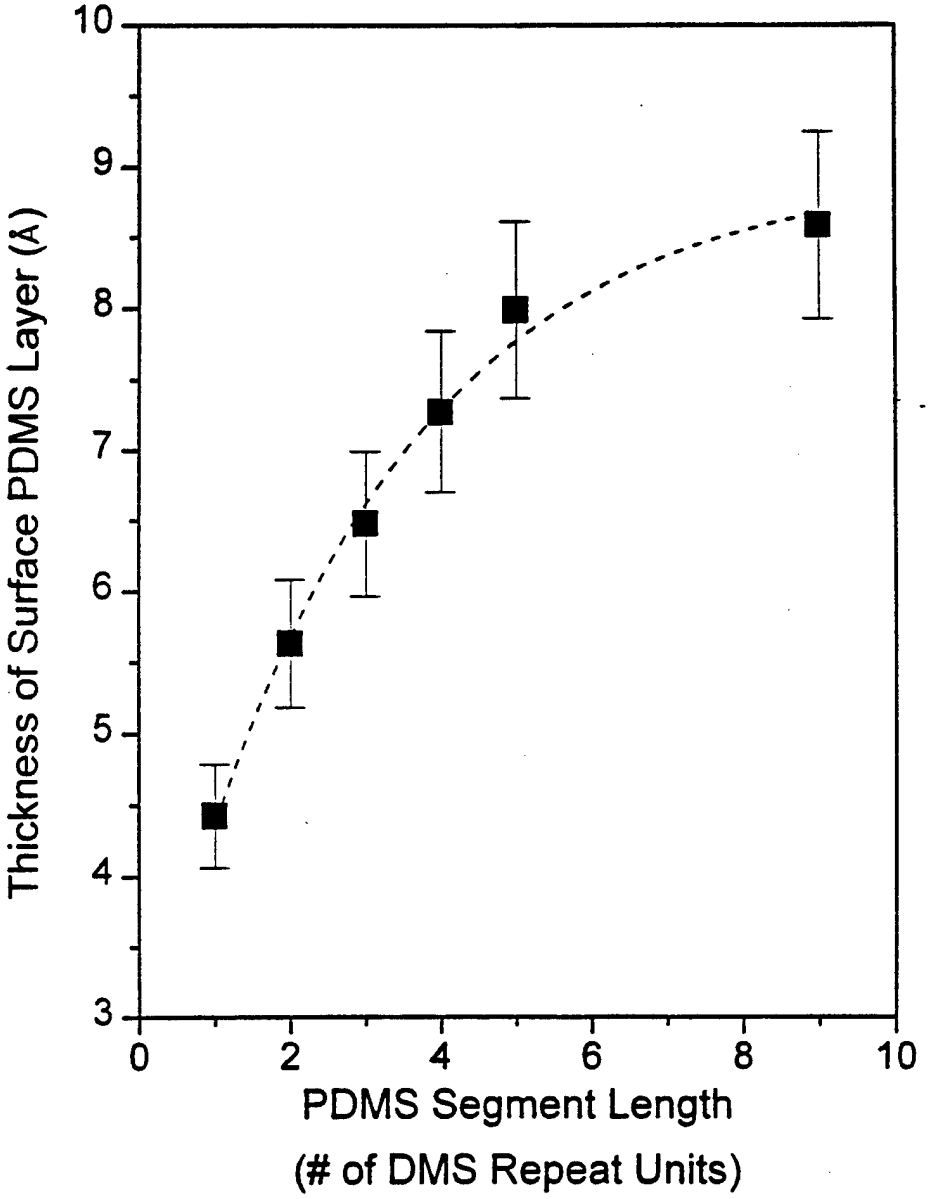
Take-off Angle (deg)	G-1	G-2	G-3	G-4	G-5	G-9
10	30.5±1.5	36.9±1.8	43.0±2.2	50.5±2.5	58.4±2.9	64.6±3.2
30	23.9±1.2	25.8±1.3	27.7±1.4	30.0±1.5	31.2±1.6	33.9±1.7
45	19.9±1.0	21.8±1.1	23.9±1.2	24.8±1.2	24.3±1.2	25.8±1.3
90	19.1±1.0	21.0±1.1	21.6±1.1	22.0±1.1	23.1±1.2	25.5±1.3

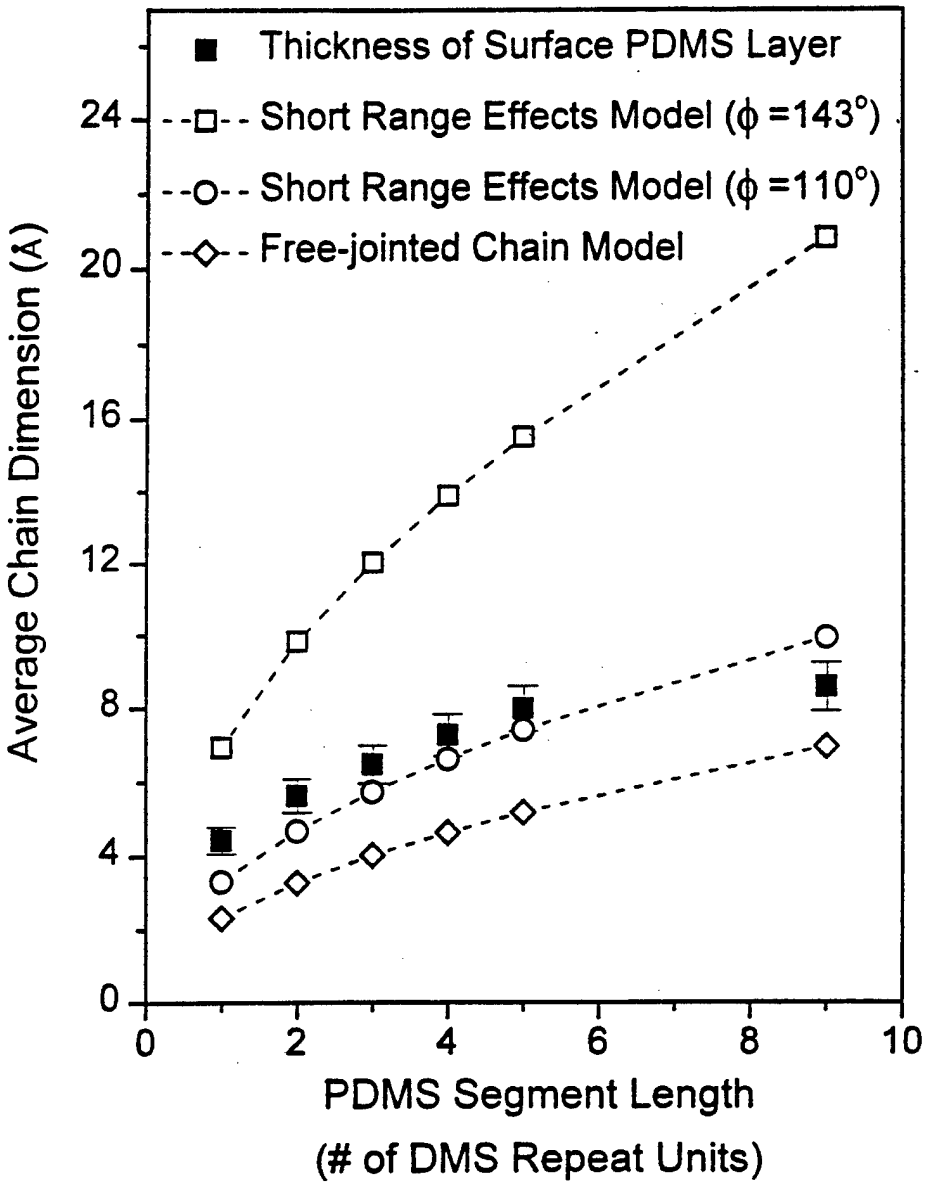


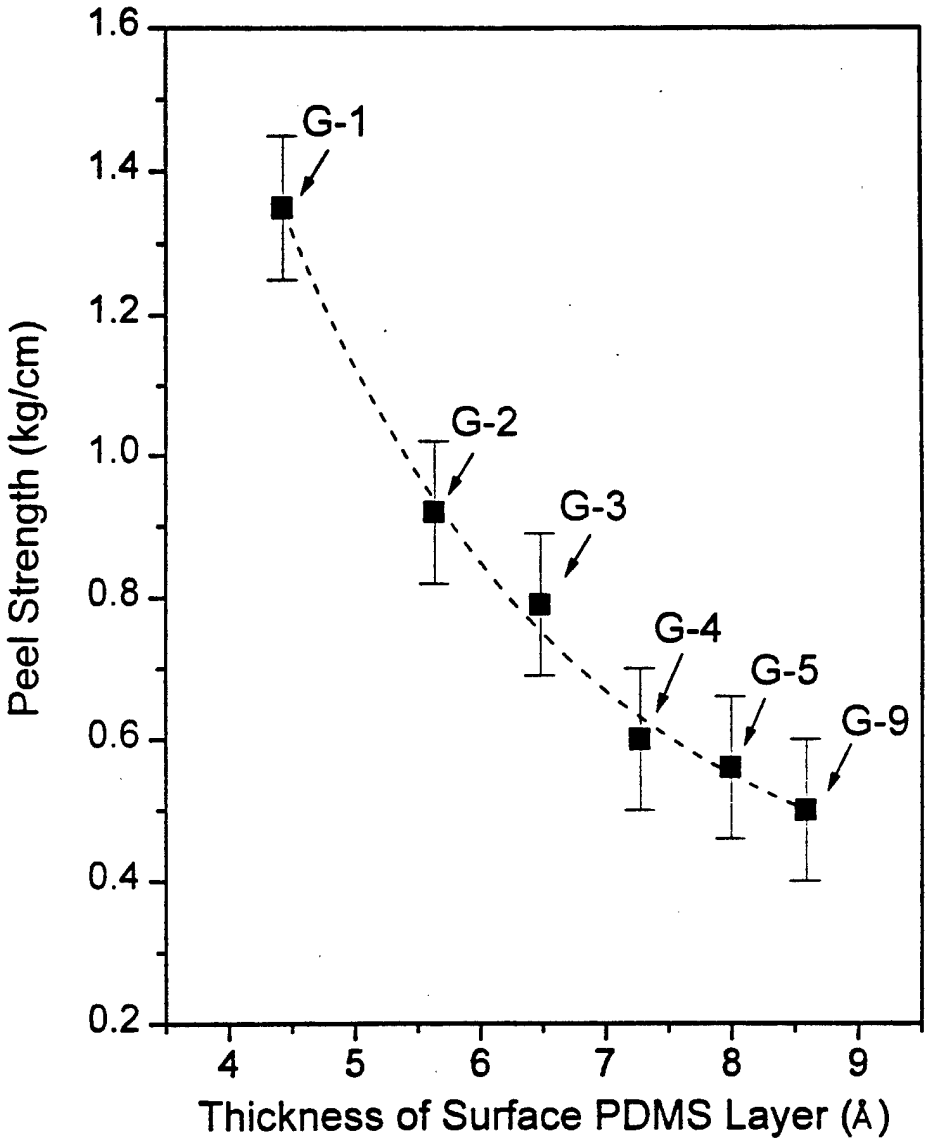
(Theta is photoelectron take-off angle)

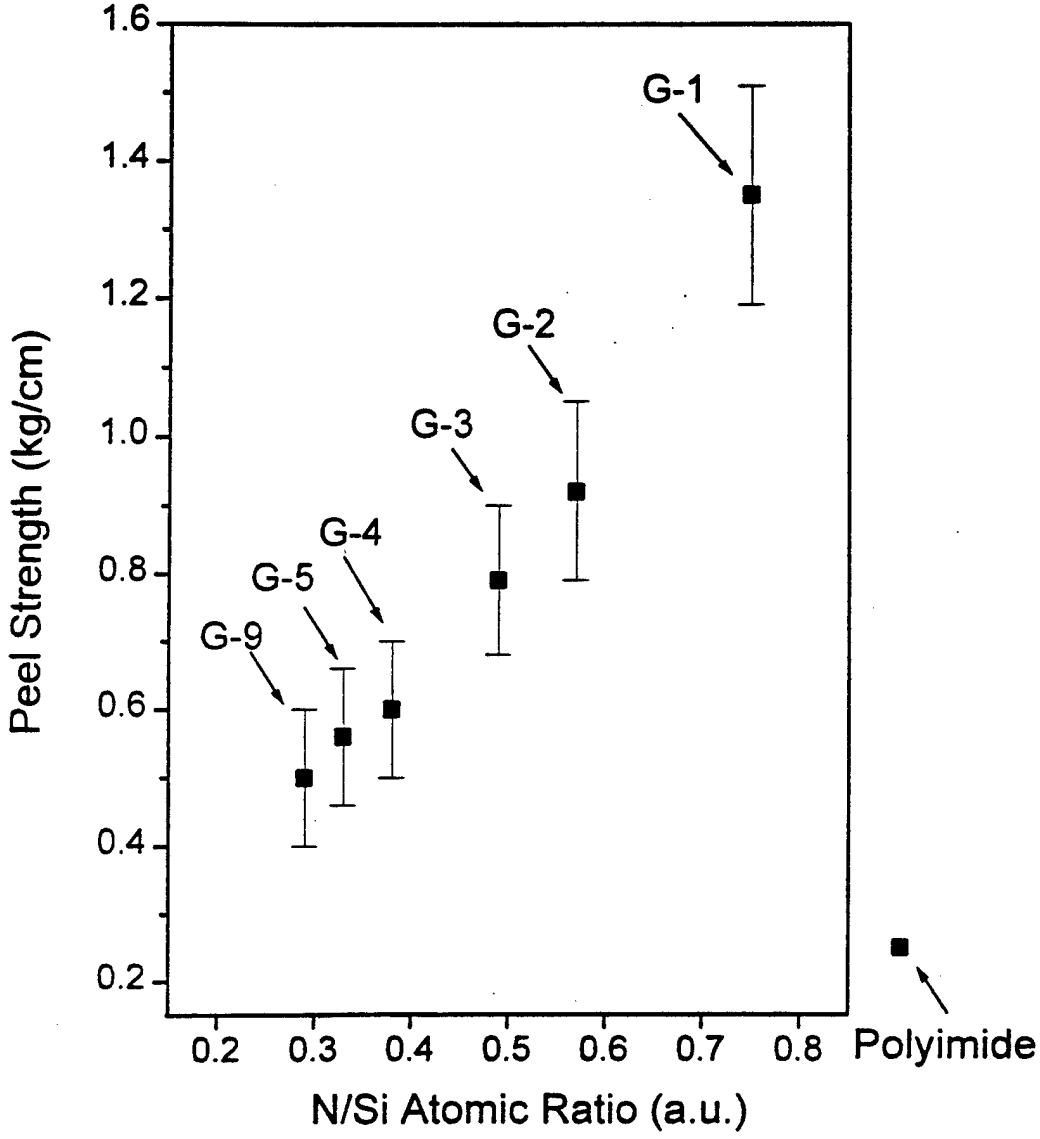

1.0
0.8
0.6
0.4
0.2
0.0
Volume Fraction of PDMS
0
10
20
30
40
50
Sampling Depth (Å)
G-1
G-2
G-3
G-4
G-5
G-9


Surface Coverage at Zero Sampling Depth
(Volume Fraction of PDMS)
1.05
1.00
0.95
0.90
0.85
0
2
4
6
8
10
PDMS Segment length
(# of DMS Repeat Units)


Thickness of Surface PDMS Layer (Å)
10
9
8
7
6
5
4
3
0
2
4
6
8
10
PDMS Segment Length
(# of DMS Repeat Units)


Thickness of Surface PDMS Layer
Short Range Effects Model (ϕ =143°)
Short Range Effects Model (ϕ =110°)
Free-jointed Chain Model
Average Chain Dimension (Å)
0
4
8
12
16
20
24
0
2
4
6
8
10
PDMS Segment Length
(# of DMS Repeat Units)


1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Peel Strength (kg/cm)
G-1
G-2
G-3
G-4
G-5
G-9
4
5
6
7
8
9
Thickness of Surface PDMS Layer (Å)


Peel Strength (kg/cm)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
G-1
G-2
G-3
G-4
G-5
G-9
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Polyimide
N/Si Atomic Ratio (a.u.)